NQR Studies of the Structure of Glasses and Crystalline Compounds *

P. J. Bray **, DongHoon Lee, De Gen Mao, and G. L. Petersen

Department of Physics, Brown University, Providence, RI USA 02912

S. A. Feller ***, D. L. Bain, D. A. Feil, Ponnappa Pandikuthira, and Sumit Nijhawan

Department of Physics, Coe College, Cedar Rapids, Iowa, USA 52402

Pure nuclear quadrupole resonance (NQR) spectroscopy at low frequencies (down to 275 kHz) has been used to investigate a number of borate, aluminate, and vanadate crystalline compounds and borate glasses. The values of the quadrupole coupling constants (Q_{cc}) and asymmetry parameters (η) are obtained with error limits that are one or two orders of magnitude less than those for values obtained from NMR spectra. New sites, not resolved in NMR spectra, have been detected for boron in borate glasses.

Introduction

A Robinson-type [1, 2] regenerative spectrometer has recently been developed [3, 4] that is very sensitive at relatively low frequencies (currently down to about 250 kHz). This instrument is being used to detect the NQR spectra of various elements (e.g. B, Al, Sc, V, Ga) in glasses and crystalline solids. Initial and recent results of these studies are reported in the following section. All of the data were obtained at 77 K unless otherwise noted.

Polycrystalline Solids

The ^{11}B NQR response for crystalline B_2O_3 at 77 K is displayed in Figure 1. The resonance, located at 1351.5 ± 0.1 kHz, has a signal-to-noise ratio (S/N) of more than 100. Since the spin of ^{11}B is 3/2, there is only one resonance, located at

$$v = \frac{Q_{cc}}{2} \sqrt{1 + \frac{\eta^2}{3}}, \qquad (1)$$

where Q_{cc} is the quadrupole coupling constant e^2qQ and η is the asymmetry parameter. The small response above 1400 kHz is one of the ^{10}B responses, and is shown in greater detail in Figure 2. The latter spectrum was obtained by running the spectrometer with a much larger gain setting than that used in obtaining the spectrum in Figure 1. Since the spin of ^{10}B is $I = 3$, there can be as many as 13 NQR responses [5] from ^{10}B in a single site in a boron-containing solid (see Figure 3). The natural isotopic abundance of ^{10}B is 18.8% as compared to 81.2% for ^{11}B.
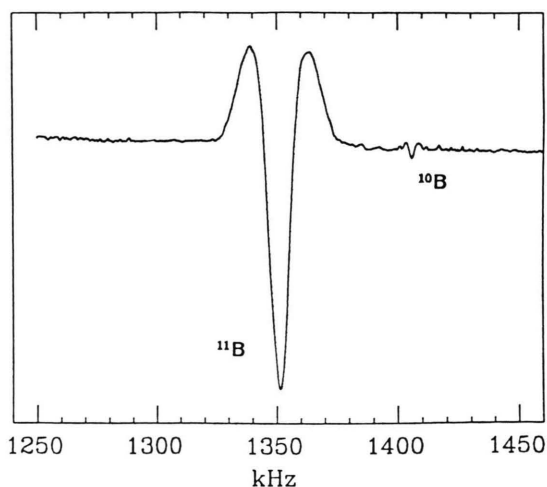
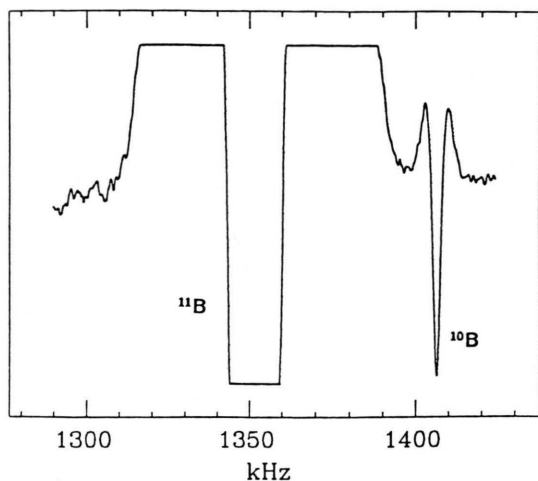Fig. 1. Boron NQR spectrum for crystalline B_2O_3.

Fig. 2. The features of Fig. 1 displayed with a greatly expanded vertical scale.
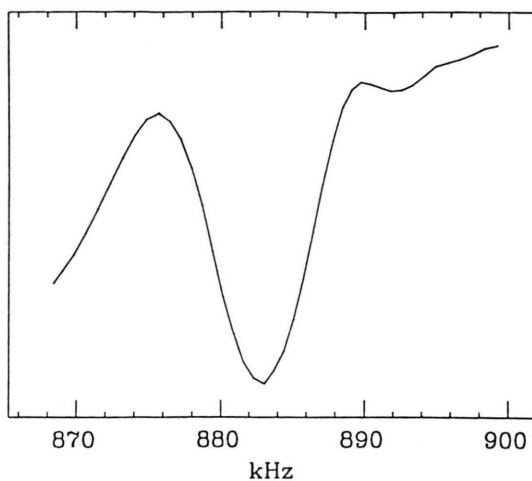

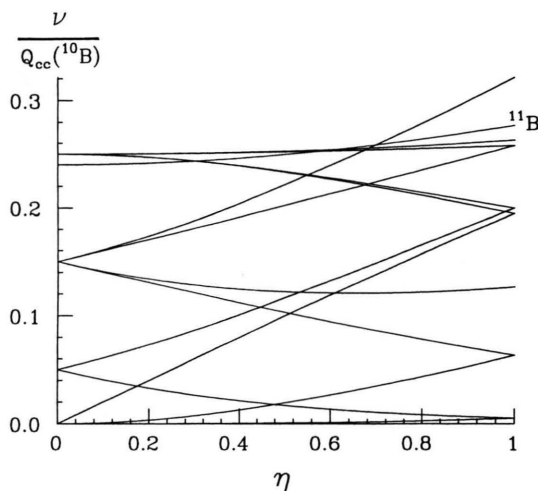Fig. 4. A ^{10}B NQR response from the spectrum for crystalline B_2O_3 at 77 K.

Fig. 3. ^{10}B (spin $I = 3$) NQR frequencies (in units of Q_{cc}).

Since (1) involves both Q_{cc} and η in the expression for the single transition frequency, values of the two parameters cannot be obtained from the ^{11}B resonance. But the observed transitions for ^{10}B (see the examples in Figs. 2 and 4) can be used with the data displayed in Fig. 3 to obtain those values. For ^{11}B in crystalline B_2O_3 one finds [4] at 77 K that $Q_{cc}(^{11}B) = 2701.1 \pm 0.2$ kHz and $\eta = 0.0669 \pm 0.0004$. The values at 300 K are 2682.6 ± 0.5 and 0.071 ± 0.001 [6]. (Note that $Q_{cc}(^{10}B)/Q_{cc}(^{11}B) = 2.084 \pm 0.002$ [4].)

The boron atoms in crystalline B_2O_3 are in the center of planar triangles of oxygens [7–9]. The

known range of Q_{cc} values for this configuration is $2.4 \leq Q_{cc} \leq 2.9$ MHz with η values generally smaller than 0.2 if the triangles are symmetric (e.g. the three oxygens are each bonded to a boron outside the triangle as in crystalline B_2O_3) and larger than 0.4 if the triangles are asymmetric (e.g. having one or two non-bridging oxygens).

The detection of many of the ^{10}B NQR transitions in a borate material is illustrated by the case of calcium metaborate [6]. Figure 5 displays eleven ^{10}B responses that are consistently present in repeated acquisitions of the NQR spectra. A fit of these resonance frequencies to the data displayed in Fig. 3 yields $Q_{cc}(^{10}B) = 5406.5 \pm 1$ kHz, $Q_{cc}(^{11}B) = 2594.3 \pm 0.5$ kHz, and $\eta = 0.515 \pm 0.001$. The boron atoms in this material are in asymmetric BO_3 triangles having two bridging and one non-bridging oxygen (Fig. 6), which gives rise to the large asymmetry parameter.

The structural units in crystalline borates (Fig. 7) are made up of BO_3 triangles and BO_4 tetrahedra; in the latter case, the boron atom is in the center of the tetrahedron of oxygens. For the four-coordinated borons, the values of Q_{cc} are low because of the tetrahedral symmetry. All of the previously reported values are such that $0 \leq Q_{cc}(^{11}B) \leq 800$ kHz. A value of 527 ± 6 kHz, with $\eta = 0.53 \pm 0.04$ has recently been deduced [4] from combined NMR and NQR ^{11}B data for ^{11}B in the tetrahedral site (see Fig. 7) in lithium diborate ($Li_2O \cdot 2 B_2O_3$). An unusual case is that of the compound $PbO \cdot 2 B_2O_3$ (lead diborate) which is known [10, 11] to contain only BO_4 units. The ^{11}B

kHz
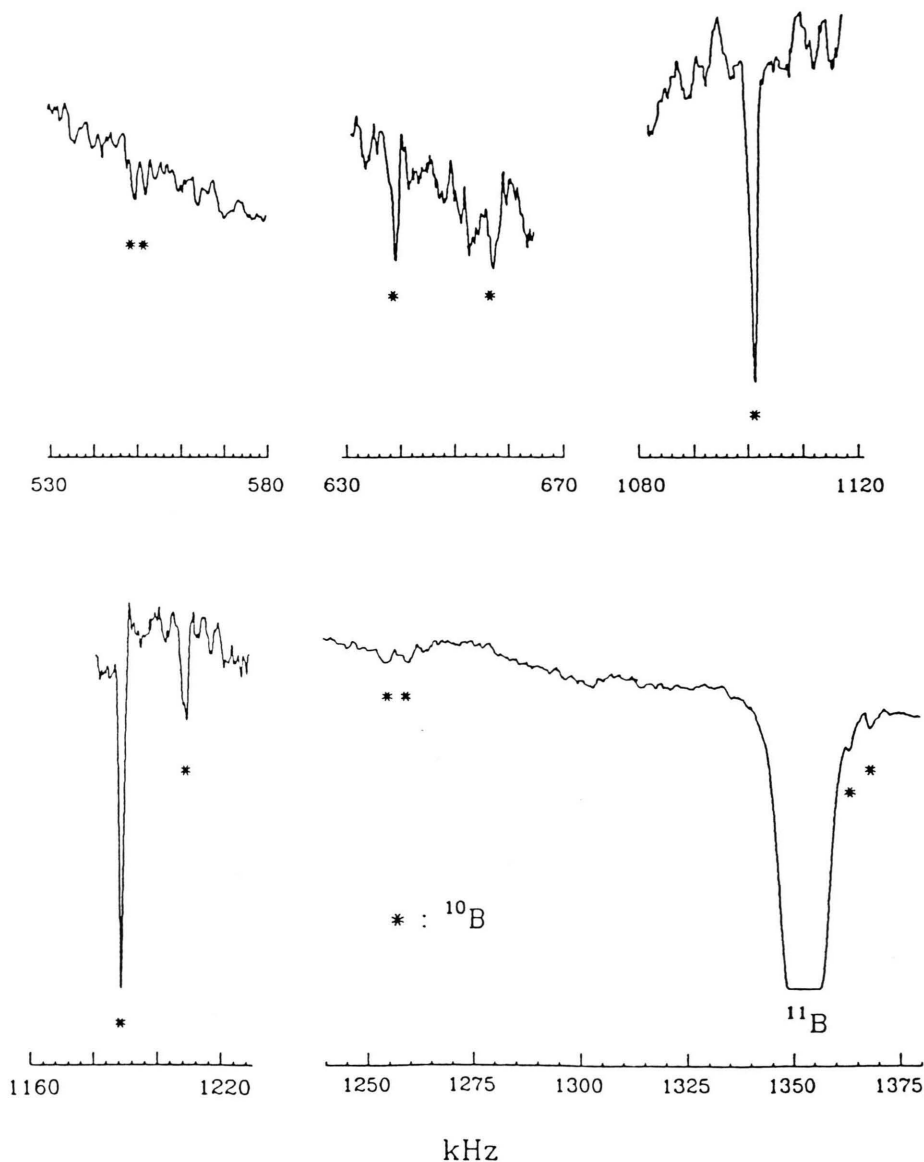
Fig. 5. ^{11}B and ^{10}B NQR spectra of $CaO-B_2O_3$ at 77 K, the ^{11}B line is driven off scale in order to show the ^{10}B lines.
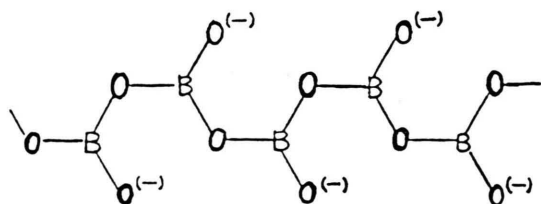
Fig. 6. A portion of the $(BO_2)_n^{n-}$ chain in calcium metaborate; the non-bridging oxygen is negatively charged.

NQR spectrum (Fig. 8) contains two responses, showing that there are two different boron sites in this material. NMR spectra for the narrow ^{11}B resonance in this material provide additional information on the quadrupolar interaction [6]. Together, the NQR and NMR date yield the values shown in Table 1. A search for ^{10}B responses in a ^{10}B-enriched sample may yield much more accurate values of Q_{cc} and η. (Most of the

Boroxol

Pyroborate

Pentaborate

Triborate

Tetraborate

Orthoborate

Diborate

Metaborate
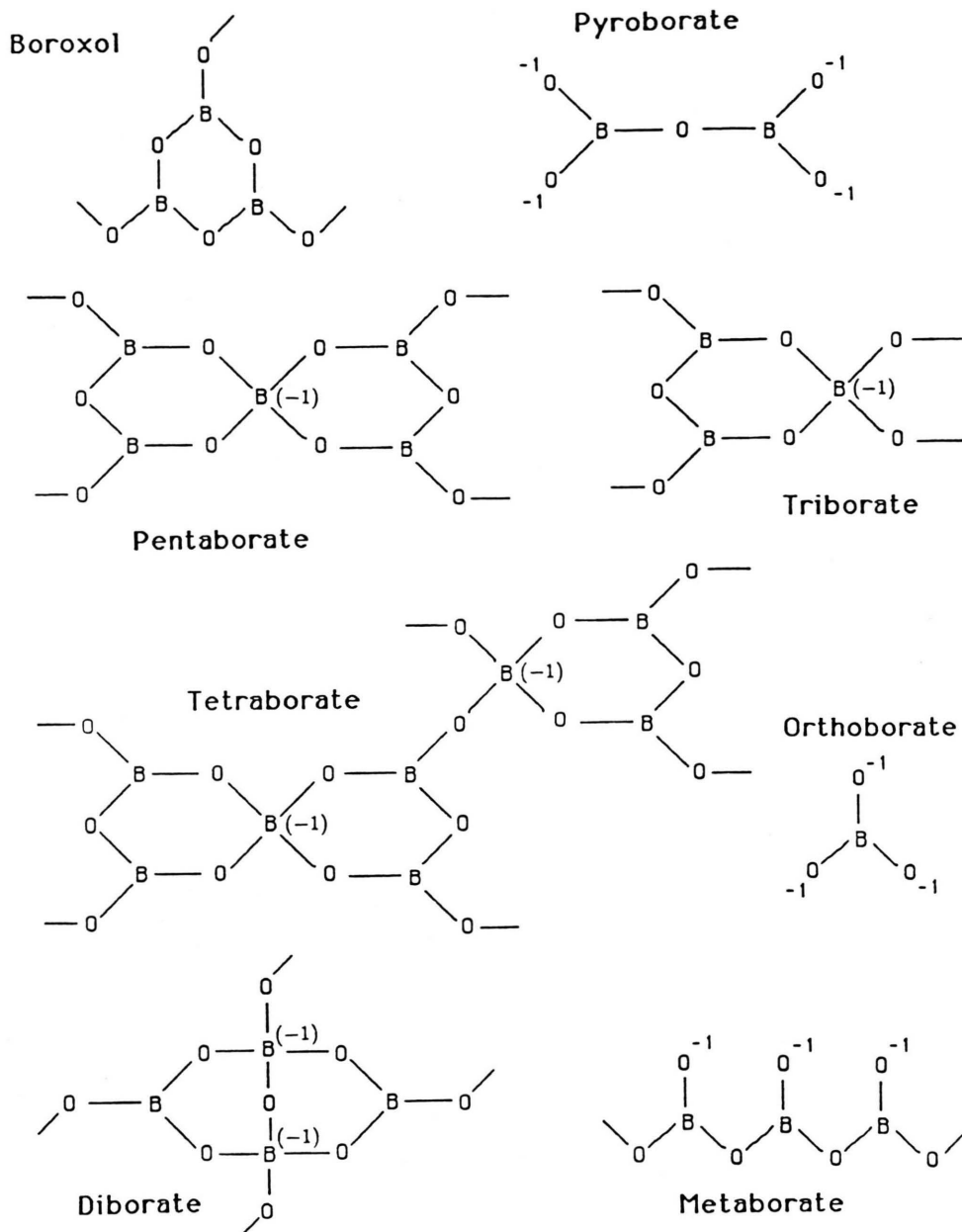
Fig. 7. Structural groupings for alkali borate compounds and glasses.

Table 1. ^{11}B quadrupole parameters for crystalline PbO · 2 B$_2$O$_3$.

BO$_4$	Q_{cc} (kHz)	η
Site 1	805 ± 5	0.90 ± 0.03
Site 2	960 ± 5	0.05 ± 0.03

^{10}B NQR responses for borates are below the ^{11}B resonance (Fig. 3) and are difficult to detect when the ^{11}B response is at a low frequency.)

^{11}B and ^{27}Al share the characteristic of being impossible or extremely difficult to detect with pulsed NQR spectrometers, apparently because of extremely
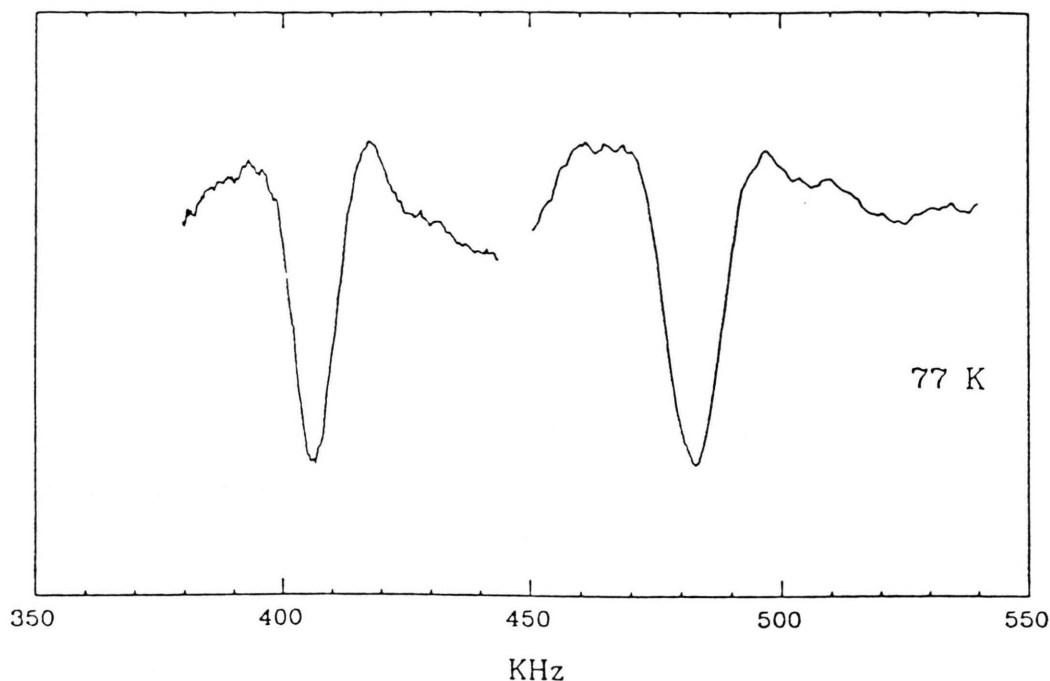
Fig. 8. ^{11}B NMR of $PbO-2B_2O_3$ at 77 K.
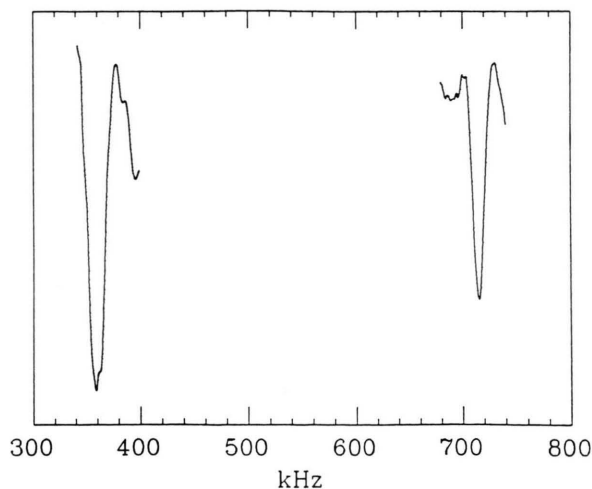
Fig. 9. [27]Al NQR response for corundum (α-Al_2O_3) at 77 K.

Table 2. [27]Al quadrupole parameters for corundum (α-Al_2O_3).

Studies	Q_{cc} (MHz)	η
NQR study	2.386 ± 0.002	0.034 ± 0.016
NMR study	$2.40 \ \pm 0.03$	0

short relaxation times. But [27]Al is just amenable as ^{11}B to detection with CW NMR instruments. Figure 9 displays the two NQR responses expected for this spin $I = 5/2$ nucleus in the single site in corundum (α-Al_2O_3). The signals are strong, even at 360 kHz, and yield the values of Q_{cc} and η displayed in Table 2. Included in Table 2 are the parameters found in an earlier NMR study [12]. Since the visible quadrupolar effects in an ^{27}Al NMR spectrum are generally of second-order, the spectrum is relatively insensitive to all but large changes in Q_{cc} and η. Clearly, much more accurate values can be obtained from the NQR responses. It is, in fact generally true that NQR can provide an increase in accuracy by an order of magnitude or more over Q_{cc} and η values obtained from the first-order or second-order effects of the quadrupolar interaction on the NMR spectrum.

NQR spectra have recently been obtained [13] for [27]Al in the three crystalline forms of Al_2SiO_5 or ($Al_2O_3 \cdot SiO_2$). Figure 10 displays the responses for the AlO_4 and AlO_6 sites in sillimanite. The frequencies yield the values given in Table 3. Similar accuracy has been attained [13] in the quadrupolar parameters for the 5- and 6-coordinated aluminum sites in andalusite and the four 6-coordinated sites in kyanite.

Table 3. ^{27}Al quadrupolar parameters for sillimanite at 77 K.

| Site	Q_{cc} (MHz)	η
AlO$_4$	6.7867 ± 0.0030	0.5254 ± 0.0011
AlO$_6$	8.7409 ± 0.0020	0.4884 ± 0.0006
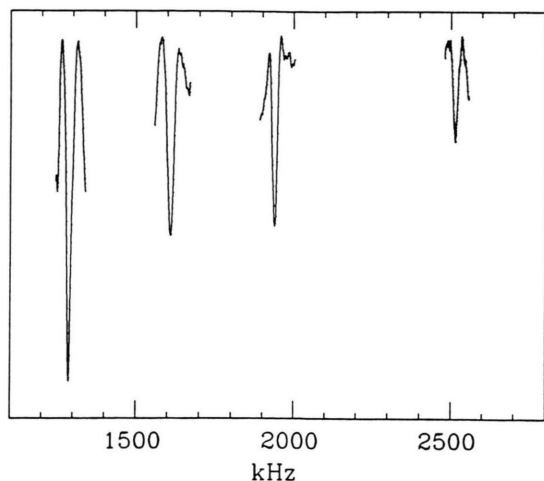
Fig. 10. ^{27}Al NQR responses for sillimanite (Al$_2$SiO$_5$) at 77 K.

The quadrupolar parameters for ^{51}V in a number of metavanadates have previously been obtained from NMR spectra [14]. More accurate values are now available from NQR measurements [6, 15]. Figure 11 displays two of the three ^{51}V responses expected for this spin $I = 7/2$ nucleus in ammonium metavanadate (NH$_4$VO$_3$). A search at higher frequencies has not detected the third response, which may then be in the 250–300 kHz region. Modification of the spectrometer will be required for satisfactory operation in that frequency region. All of the responses have been detected in the sodium and potassium metavanadates. Table 4 summarizes the data for the three compounds studied.

Included in Table 4 are values of Q_{cc} and η previously determined [14] from a ^{51}V NMR study. The large improvement in accuracy achieved using NQR is apparent. (The lower accuracy of NQR-derived values for NH$_4$VO$_3$ reflects the fact that only two NQR responses were detected.)

Glasses

NMR has been used for some 35 years to investigate the studies of glasses [16], with much attention
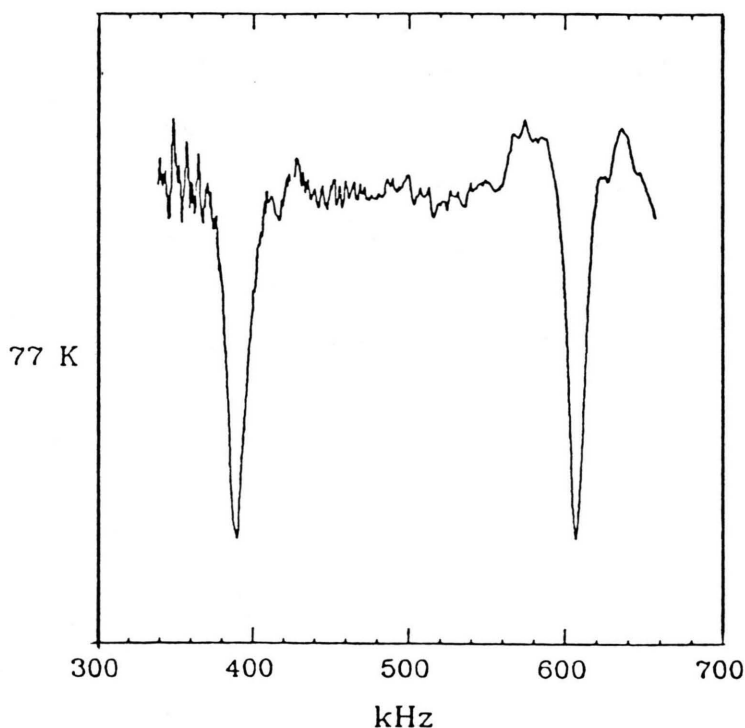
Fig. 11. ^{51}V NQR of NH$_4$VO$_3$ at 77 K.
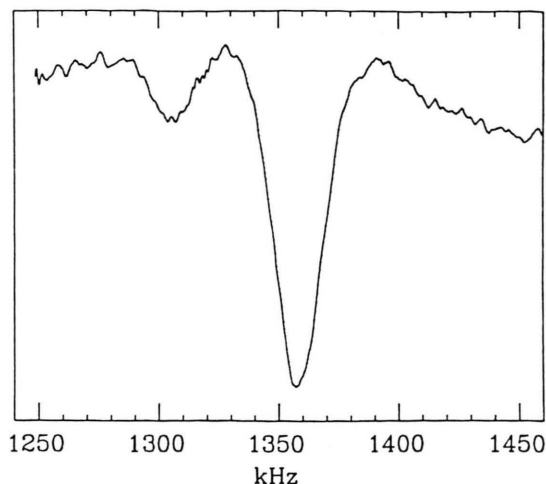
Fig. 12. ^{11}B NQR responses from vitreous B_2O_3 at 77 K.
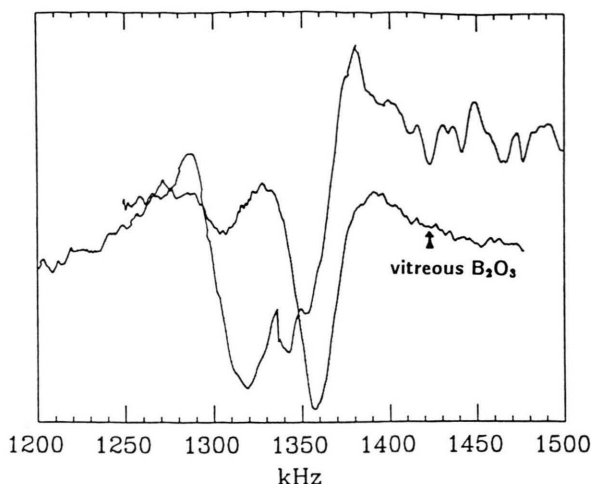
Fig. 13. ^{11}B NQR for a glass of composition $0.15\,Na_2O-B_2O_3$ referenced to vitreous B_2O_3 at 77 K.

Table 4. ^{51}V quadrupole parameters for three metavanadates.

Q_{cc} (kHz) η	NMR (300 K)	NQR (300 K)	NQR (77 K)
KVO_3	4360 ± 60 75 ± 0.10	4201 ± 2 0.794 ± 0.001	4207 ± 2 0.877 ± 0.001
$NaVO_3$	3650 ± 60 0.60 ± 0.10	3745 ± 3 0.489 ± 0.003	3725 ± 2 0.587 ± 0.001
NH_4VO_3	2880 ± 60 0.30 ± 0.10	2975 ± 20 0.437 ± 0.020	2868 ± 5 0.363 ± 0.013

focusing on ^{11}B and ^{10}B spectra for borate glasses [17]. But low-frequency NQR studies can now yield quadrupolar parameters of much higher accuracy and obtain data not available from NMR studies (e.g. Q_{cc} and η for borons in tetrahedral BO_4 units for which $0 \leq Q_{cc} \leq 800$ kHz.)

Figure 12 displays the two ^{11}B responses for vitreous boron oxide (B_2O_3). The responses are unexpectedly narrow (widths ≤ 30 kHz) in light of the broad distribution in the values of the electric field gradient (EFG) components and Q_{cc} values expected for glasses. (The single feature most commonly used to describe the difference between crystalline and vitreous states of matter is the random arrangements of atoms and chemical bonds in glasses.) The only previous NQR study [18] of glasses involved ^{75}As in arsenic chalcogenides revealed linewidths of 7 MHz or more, precluding resolution of resonances from different sites. In contrast to the distribution in Q_{cc} values of 10% in

As$_2$S$_3$, the distribution smaller than 2% in borate glasses.

The larger of the two responses in Fig. 12 is quite near the location of the single ^{11}B response for crystalline B_2O_3 (see Fig. 1) and is believed to arise from BO_3 units in boroxol structural groupings (see Fig. 7), which have been identified by some investigators [19, 20] as the principal structural groupings in the glass. The smaller response may arise from BO_3 in other borate structural groupings (see Figure 7).

The pioneering explorer of borate structures by infrared spectroscopy, Jan Krogh-Moe [21] proposed a structural model of borate glasses as consisting of mixtures of the structural groupings (Fig. 7) from the crystalline compounds. This is a significant modification of the conventional random network model which would envision a random arrangement of BO_3 and BO_4 units in the glass. The current NQR studies of borate glasses are focused on assessing the validity of the Krogh-Moe model. Figure 13 displays the ^{11}B spectrum [22, 23] for a glass of molar composition $0.15\,Na_2O-B_2O_3$, along with the spectrum from Fig. 12 for pure vitreous B_2O_3. There are clearly at least three peaks in the sodium borate glass, of which two may be the same as those found in vitreous B_2O_3. [One would not expect to find exact agreement of the frequencies for BO_3 units in structural groupings common to the crystalline compounds (e.g. boroxol, tetraborate, diborate; see Fig. 7) and the glasses. The randomness in the glass structure would arise from random bondings among the various structural
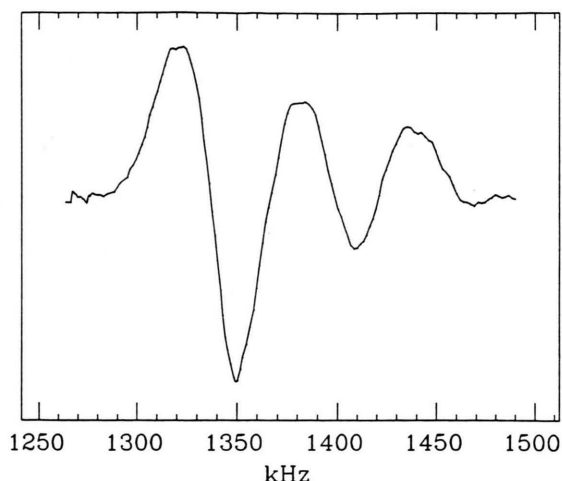
Fig. 14. ^{11}B NQR responses for vitreous $2\,Na_2O - B_2O_3$ at 77 K.

Fig. 15. ^{11}B NQR response from BO_4 units in polycrystalline lithium diborate ($Li_2O \cdot 2\,B_2O_3$) at 77 K.

Fig. 16. NQR responses for vitreous $Li_2O - B_2O_3$ in the 700 kHz region at 77 K.

groupings in a glass, giving rise to some alterations in the EFG's (and thus the Q_{cc} values) for the borons in the groupings. This would produce the distributions of Q_{cc} values in the glasses (which produce the wider lines in the glasses as compared to the crystals; compare Figs. 1 and 12) and could produce shifts in the peak frequencies comparable to the linewidths for the glasses.] Earlier NMR studies [24] of lithium borate glasses by NMR, with analysis of the spectra based on the Krogh-Moe model, would predict the presence of boroxol, tetraborate, and diborate groupings in the $0.15\,Na_2O - B_2O_3$ glass. NQR spectra for glasses spanning the region of glass formation in the $Na_2O - B_2O_3$ and $Li_2O - B_2O_3$ systems, and for all of the crystalline compounds in those systems, are currently being secured, so that comparisons of the ^{11}B resonance frequencies for the glasses and crystals can be made. If the degree of correspondence favors the Krogh-Moe model, the ^{10}B spectra for ^{10}B-enriched samples will be secured for a comparison of the highly accurate values of Q_{cc} and η.

Figure 14 displays ^{11}B NQR responses for BO_3 in a sodium pyroborate glass ($2\,Na_2O \cdot B_2O_3$). The Krogh-Moe model would predict the pyroborate structural grouping to be dominant in this glass, with some orthoborate and metaborate groupings. Q_{cc} for the orthoborate groubing is known [25] to be larger than the Q_{cc} values for other groups. One tentatively assigns, then, the lower frequency response to the pyroborate grouping and the one above 1400 kHz to the orthoborate.
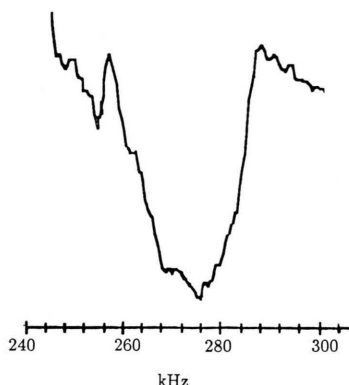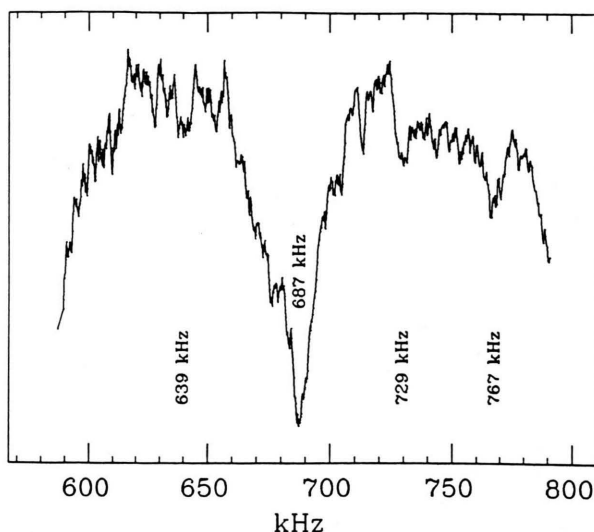
The ^{11}B response from BO_3 units reflects the observation that $2.4 \leq Q_{cc} \leq 2.9$ MHz for all borates investigated by NMR and NQR. NQR responses can occur, then, in the region from about 1200 to 1675 kHz (see (1)). The NQR spectra for BO_4 units may provide an even more accurate identification of structural groupings in glasses since the accumulated NMR data yield $0 \leq Q_{cc} \leq 800$ kHz for BO_4 units in borate structural groupings. With the detection of the ^{11}B NQR responses in the 400–500 kHz region for crystalline $PbO \cdot B_2O_3$ (Fig. 8), this range is appropriately ex-

tended so that $0 \leq Q_{cc} \leq 1100$ kHz. This broad range presumably reflects the sensitive dependence of the quadrupolar parameters to distortions (asymmetries) of the BO_4 tetrahedra. Those distortions can vary strongly among BO_4 units in different structural groupings. The ^{11}B NQR response near 275 kHz for the BO_4 units in crystalline $Li_2O \cdot 2B_2O_3$ is shown in Figure 15. Modifications of the NQR spectrometer (currently in progress) to achieve greater sensitivity at low frequencies should yield spectra down to or below 150 kHz.

The range of values for Q_{cc} in BO_4 units must apparently be extended to even larger values based on the recent discovery [26, 27] of a ^{11}B resonance at 687 kHz in vitreous lithium metaborate (Figure 16). (The other possible responses in Fig. 16 may arise from ^{10}B.) From (1), the Q_{cc} value for this response lies between 1190 and 1374 kHz. Identification of the unit responsible for this resonance has not been made, but there are reasons to postulate a BO_4 unit with a non-bridging oxygen, which would constitute an exception to the general Krogh-Moe model.

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